



Recent progress in photocatalytic conversion of carbon dioxide over gallium oxide and its nanocomposites

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Photocatalytic conversion of CO₂ is a promising method to solve problems of both energy crisis and global climate change. The efficient transfer of solar energy into high-value chemical energy is the ultimate goal of this technology. Gallium oxide is a suitable candidate for the photocatalytic conversion of CO₂ due to its ideal band positions. Modification of Ga₂O₃ to achieve enhanced photocatalytic activity and understanding the catalytic mechanism are important for the design of high-efficiency photocatalysts.

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Introduction

The global energy crisis is continually growing due to the use of non-renewable energy sources, such as fossil fuels. Consequently, excessive carbon dioxide (CO₂) from the consumption of these fossil fuels are released into the atmosphere. This directly exacerbates the greenhouse effect and global warming [1]. It is of great urgency to solve both the energy crisis and global warming and thus mitigate environmental and economic disasters. Therefore, the development of renewable energy technologies is essential for a reliable and sustainable energy supply [2]. Sunlight is the most abundant renewable energy source as it is clean, non-monopolized, and environmentally friendly. Harvesting, storage, and practical utilization of solar energy are critical worldwide issues that must be overcome for the widespread adoption of solar energy [3]. Recently, the capture, storage, and utilization of CO₂,

directly or indirectly, using solar energy have been attempted to mitigate CO₂ emissions and solve energy crisis simultaneously [4].

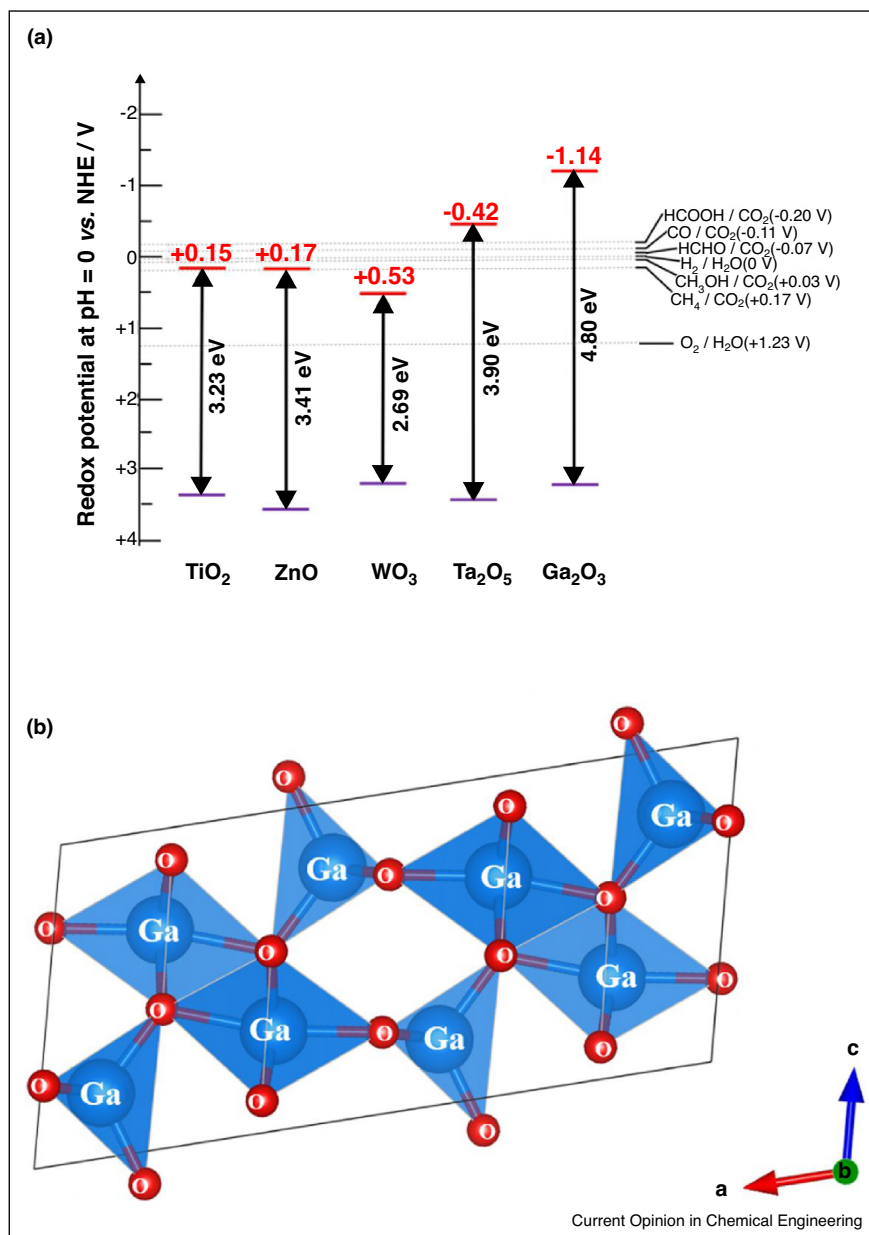
The photocatalytic conversion of CO₂ to chemical feedstocks and hydrocarbon-based fuels is a promising method to simultaneously alleviate the global energy crisis and global warming [5]. Specifically, the photocatalytic conversion of CO₂ using H₂O as an electron donor by heterogeneous catalysts would be ideal, but achieving efficient catalysis under these conditions has proven to be of great challenges. This reaction is an uphill reaction, taking the conversion of CO₂ using H₂O to CO, O₂ and H₂ as an example, the standard Gibbs free energy change (ΔG°) of this reaction is +270 kJ mol⁻¹. Therefore, solar energy can be converted and stored as chemical energy. Because of the uphill barriers, this reaction is more difficult to achieve as compared to traditional photocatalytic degradation reactions, which normally are downhill reactions ($\Delta G^\circ < 0$) [6]. To date, developments in the photocatalytic conversion of CO₂ are still at a very early stage. Nevertheless, a variety of photocatalysts have been developed that achieve the conversion of CO₂ by H₂O to carbon monoxide (CO), formic acid (HCOOH), formaldehyde (HCHO), methanol (CH₃OH), and methane (CH₄) [7].

As a representative photocatalyst, gallium oxide (Ga₂O₃) has been recently investigated for the photocatalytic conversion of CO₂. Generally, Ga₂O₃ exists as polymorphs α -, β -, γ -, δ -, and ϵ [8,9]. Among these polymorphs, β -Ga₂O₃ has been widely investigated due to its thermodynamically stability [10,11]. β -Ga₂O₃ is a semiconductor with a wide band gap of ~4.8 eV. The conduction band (CB) position of β -Ga₂O₃ is much more negative than other selected metal-oxide photocatalysts, such as TiO₂, ZnO, WO₃, and Ta₂O₅ (Figure 1a) [12–15]. This makes β -Ga₂O₃ to be promising for the photocatalytic conversion of CO₂ because it can provide more negative potential for reduction of CO₂ than others. In this short review, we will discuss the use of β -Ga₂O₃ and its modification for the photocatalytic conversion of CO₂.

Brief introduction of Ga₂O₃ and its preparation methods

Various methods have been used for the fabrication of Ga₂O₃ nanoparticles, such as sol–gel method [16], chemical vapor deposition (CVD) [17], precipitation method

Figure 1



(a) Conduction (red) and valance (purple) band positions (at pH = 0 versus NHE) of the selected oxide photocatalysts. The values adapted from Ref. [12–15]. **(b)** is the crystal structure of β -Ga₂O₃ from Ref. [23].

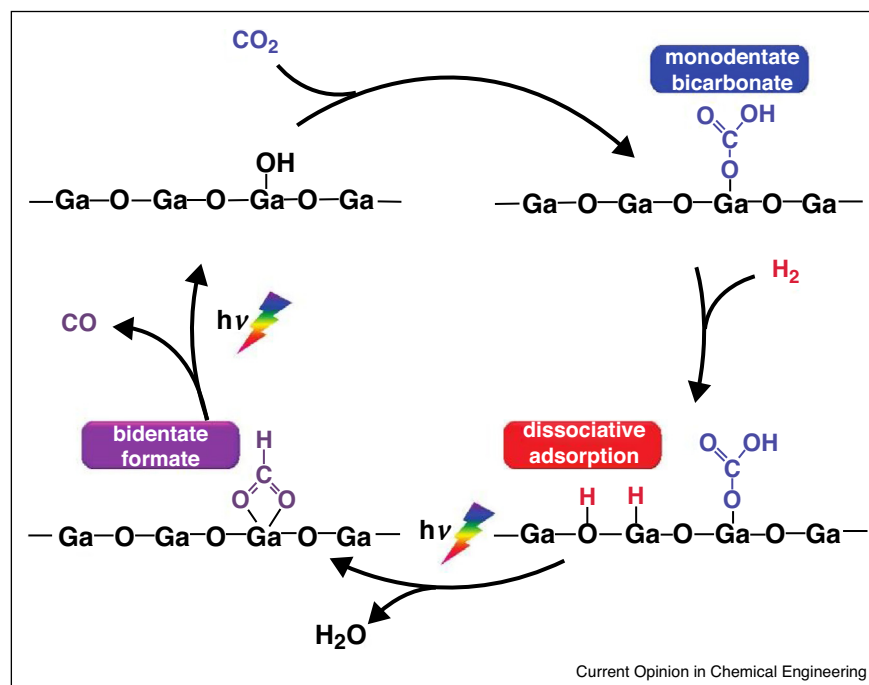
[18], and hydrothermal method [19,20]. Ga₂O₃ powder used for the photocatalytic conversion of CO₂ is usually fabricated by the calcination of the precursor of co-precipitated gallium nitrate and ammonia solution [21,22]. This process allows for the formation of β -Ga₂O₃, which contains tetrahedral and octahedral Ga ions (Ga³⁺) in its structure (Figure 1b) [23]. Tetrahedral Ga³⁺ is believed to form Lewis acid sites [24], other polymorphs such as α -Ga₂O₃ with only octahedral Ga³⁺ structure cannot form Lewis acid sites [9]. Typically, the fabricated Ga₂O₃

comprises irregular nanoparticles with elliptical rod-shaped and/or spindle-like morphologies. The Brunauer–Emmett–Teller (BET) specific surface areas of these Ga₂O₃ particles have been reported to be ~10–40 m² g⁻¹ [20,25,26,27].

Photocatalytic conversion of CO₂ using CH₄ or H₂ as an electron donor

Ga₂O₃ has been investigated as an active catalyst for the hydrogenation of CO₂ for more than 20 years [28–30].

Figure 2



Schematic mechanism of photocatalytic conversion of CO_2 over Ga_2O_3 in the presence of H_2 . Reprinted with permission from Ref. [33**]. Copyright (2010) American Chemical Society.

However, the first successful photocatalytic conversion of CO_2 using a Ga_2O_3 catalyst was reported by Yuliati *et al.* [31], who demonstrated the photocatalytic conversion of CO_2 using CH_4 as an electron donor with a 300 W Xe lamp irradiation. H_2 and CO were the main products of this reaction. In this system, the input of thermal energy is necessary to achieve CO_2 dry reforming of methane (DRM). Therefore, this report can be classified as thermal-photocatalytic processes for the conversion of CO_2 .

In late 2008, Teramura *et al.* [21*] reported the first example of the Ga_2O_3 photocatalytic conversion of CO_2 using H_2 as an electron donor with a 200W Hg–Xe lamp irradiation. CO was the only detected reduction product of CO_2 . $\alpha\text{-Ga}_2\text{O}_3$, $\beta\text{-Ga}_2\text{O}_3$, and $\gamma\text{-Ga}_2\text{O}_3$ were all reported to show photocatalytic activity toward the conversion of CO_2 using H_2 as an electron donor. Of the various polymorphs, $\beta\text{-Ga}_2\text{O}_3$ calcined at 1073 K showed the highest catalytic activity in the study. The conversion efficiency of CO_2 was approximately 3%, and it was found that the adsorption of H_2 onto the $\beta\text{-Ga}_2\text{O}_3$ particles enhanced the photocatalytic activity. In 2011, Ahmed *et al.* [32] reported that commercial Ga_2O_3 , containing mainly α phase, showed photocatalytic activity for the formation of CO , with H_2 as an electron donor.

Tsuneoka *et al.* [33**] investigated the adsorbed species of CO_2 and H_2 on Ga_2O_3 for the photocatalytic conversion of

CO_2 with a 200W Hg–Xe lamp irradiation using Fourier transform infrared spectrometer (FT-IR) (Figure 2). Monodentate bicarbonate species were found to be reduced by the dissociatively adsorbed H_2 under photoirradiation on the surface of the Ga_2O_3 particles. The decomposition of the generated bidentate formate on Ga_2O_3 resulted in the formation of CO during photoirradiation. The dissociatively adsorbed H_2 on the Ga_2O_3 particles is key for enhancing the photocatalytic activity for the conversion of CO_2 .

Photocatalytic conversion of CO_2 using H_2O as an electron donor

When H_2O is used as an electron donor, oxidation of H_2O to yield protons and molecular oxygen is necessary for the photocatalytic conversion of CO_2 . However, water splitting is preferable in terms of energy production than that of conversion of CO_2 . Therefore, H_2 is usually the main reduction product, even in the presence of CO_2 [34]. When CO_2 is converted to CO , the selectivity toward CO evolution can be expressed as follows:

$$\text{Selectivity toward CO (\%)} = 100 \times \frac{2R_{\text{CO}}}{2R_{\text{CO}} + 2R_{\text{H}_2}}$$

where R_{CO} and R_{H_2} represent the rates of CO , H_2 , and O_2 formation, respectively. If other reduction products are

formed, their formation rates multiplied by the number of consumed electrons should be added to the numerator and denominator. Bare Ga₂O₃ was reported to show photocatalytic activity for the conversion of CO₂ to CO in and by H₂O with *c.a.* 6–14% selectivity toward CO evolution. The formation rates of CO were also limited to a few $\mu\text{mol h}^{-1}$ or less [22,35,36]. These results indicate that water splitting to H₂ occurs as the main reaction even in the presence of CO₂. Thus, the modification of the Ga₂O₃ particles is necessary to achieve enhanced selectivity and photocatalytic activity for the conversion of CO₂ using H₂O as an electron donor.

Bulk Ga₂O₃ shows limited catalytic activity due to the small amount of photocatalytic active sites due to the small BET surface area, which in turn results from high-temperature calcination. Park *et al.* [25] designed highly porous bulk Ga₂O₃ to overcome this limitation, and the fabricated highly porous Ga₂O₃ showed high CO₂ affinity. Moreover, it was found that CH₄ was the major product of conversion of CO₂ with H₂O vapor using a 300 W Xe lamp irradiation. Larger surface areas and adsorption capacity are thought to be the reason for the enhanced photocatalytic activity compared to that of bulk Ga₂O₃.

Co-catalysts are important for promoting the separation and migration of photogenerated electrons and holes [37], activation of the adsorbed CO₂ [38], and directing the production of reduction products [39]. The activity and selectivity toward the photocatalytic conversion of CO₂ in H₂O are enhanced using various types of co-catalysts [40]. Ag is one of the most effective co-catalysts for achieving high activity and selectivity toward CO evolution. Both the activity and selectivity are enhanced when Ag is used as a co-catalyst loaded on Ga₂O₃ [22,35,36].

Recently, Yamamoto *et al.* [35,41] found that small Ag clusters on Ga₂O₃ showed increased activity and selectivity toward CO evolution with a 300 W Xe lamp irradiation. They demonstrated that smaller Ag clusters accepted more electrons in their d-orbitals as result of the strong interaction with the Ga₂O₃ surface. The FT-IR results showed that Ag promoted the transformation of bidentate carbonates to form bidentate formates under photoexcitation. Further investigation indicated that structure of the Ag co-catalyst on the surface of Ga₂O₃ showed aggregation, and that partial Ag⁺ were converted to metallic Ag⁰ [36]. These changes resulted in a significant effect on the photocatalytic activity and selectivity toward CO evolution. In addition, the same group reported that the coexistence of the γ -phase and β -phase of Ga₂O₃ showed higher activity for CO production without Ag co-catalyst as compared that with the Ag co-catalyst [42]. It was proposed that the original crystalline structure is changed with the loading of Ag, which deactivates the photocatalytic activity. It should be noted that this was not the case for pure β -phase Ga₂O₃ where the loading of Ag resulted

in significantly enhanced photocatalytic activity and selectivity toward CO evolution.

Pan *et al.* [20] reported that Pt-nanoparticle-dispersed Ga₂O₃ nanoparticles showed good photocatalytic activity for CO₂ conversion in H₂O in a closed system with a 300 W Xe lamp. The highest formation rates of CO, H₂, and O₂ achieved were 21.0, 36.2, and 7.9 $\mu\text{mol h}^{-1}$, respectively, resulting in a selectivity toward CO of 36.7%. The selectivity toward CO showed significant enhancement compared to that of bare Ga₂O₃. Tiny amounts of CH₄, CH₃OH, HCHO, and HCOOH were also detected as reduction products in addition to CO.

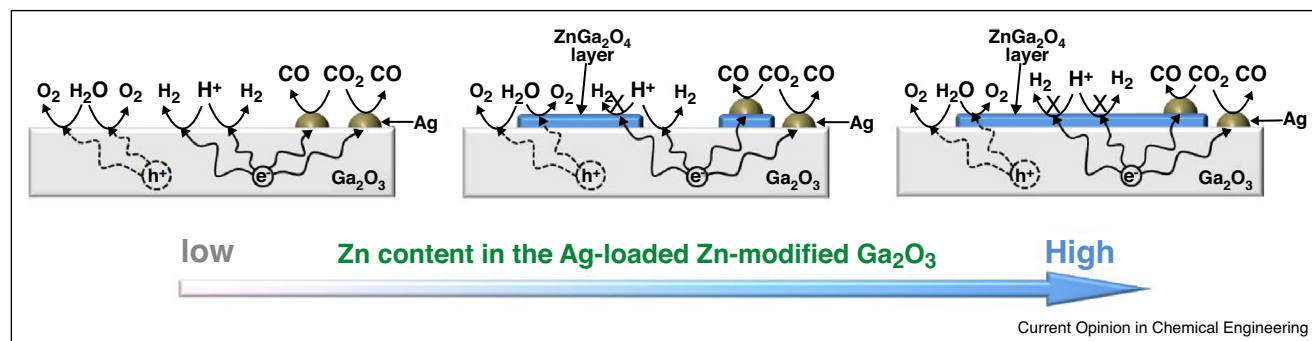
Ga₂O₃ nanocomposites for the enhanced photocatalytic activity

Even in the presence of a co-catalyst, the activity and/or selectivity toward CO evolution in the photocatalytic conversion of CO₂ by H₂O over Ga₂O₃ is limited. Therefore, further modification of Ga₂O₃ is necessary to achieve higher activity and selectivity. Because Ga₂O₃ has a wide band gap, the conductivity band (CB) and valance band (VB) positions are not limitations in the reduction of CO₂ and oxidation of O₂ (Figure 1a). The suppression of H₂ generation, increasing the ability of CO₂ adsorption and increasing active sites for the conversion of CO₂ are important for achieving enhanced photocatalytic activity and selectivity.

Wang *et al.* [43] reported the use of Ga₂O₃ modified with ZnGa₂O₄ nanoparticles as a heterojunction photocatalyst for the conversion of CO₂ to CH₄ with H₂O vapor in a closed system with a UV-enhanced (200–350 nm) 300 W Xenon arc lamp irradiation. This heterojunction photocatalyst showed higher photocatalytic activity for the production of CH₄ compared with that of the bare Ga₂O₃ and ZnGa₂O₄. It was concluded by the authors that the formation of the heterojunction improved the separation of photogenerated electron-hole pairs resulting in increased selectivity toward CH₄ evolution.

Teramura *et al.* [22] succeeded in designing a highly selective photocatalytic conversion of CO₂ to CO in and by H₂O over Ag modified, Zn-doped Ga₂O₃ in a continuous flow system using a 400 W Hg lamp. The selectivity toward CO was enhanced from 26.4 to 87.4% by doping with 3.0 mol% of Zn in Ga₂O₃. Molecular O₂ was stoichiometrically evolved, moreover, isotopic labeling experiments showed that the formed ¹³CO originated from the introduced ¹³CO₂. These results clearly showed that H₂O acts as an electron donor during the photocatalytic conversion of CO₂, which is important as overall water splitting to produce H₂ are common when using H₂O as an electron donor [44,45]. Further investigations revealed that the selectivity toward CO over H₂ can be controlled by varying the amount of Zn dopant in the Ga₂O₃ [26^{••}]. It was confirmed that a ZnGa₂O₄ layer was generated on the surface of the Ga₂O₃ by the addition of

Figure 3



Proposed mechanism for the photocatalytic conversion of CO₂ in and by H₂O over Zn modified Ga₂O₃ with changing Zn content. Reproduced from Ref. [26**] with permission from The Royal Society of Chemistry.

Zn species. The ZnGa₂O₄ layer suppresses the reduction of H⁺, significant enhancing the selectivity toward CO with increased Zn content (Figure 3). Since the formation rate of O₂ was suppressed with the inclusion of ZnGa₂O₄, this indicates that suppress H₂ is the major function of ZnGa₂O₄. This result is different than that of the reported ZnGa₂O₄/Ga₂O₃ heterojunction by Wang *et al.* [43].

Based on these preliminary studies, Teramura *et al.* [46*] investigated the intermediate species formed during the photocatalytic conversion of CO₂ by H₂O over Ag modified ZnGa₂O₄/Ga₂O₃. They found that the partial pressure of CO₂, the concentration of NaHCO₃ additives, and the reaction temperature significantly affected the photocatalytic activity and selectivity toward CO evolution. There are significant correlations between the concentration of dissolved CO₂ species and the formation rates of CO. However, no obvious relationship was observed between the catalytic activities and other kinds of species, such as carbonic acid, bicarbonate, or carbonate ions. The FT-IR results indicated that bicarbonate species were formed when CO₂ molecules bind to the hydroxyl groups on the surface of ZnGa₂O₄/Ga₂O₃. Among the bicarbonate species, mono-dentate bicarbonate is preferentially reduced to a bidentate formate intermediate by the electrons generated under photoirradiation. CO is then evolved from the decomposition of the generated formate.

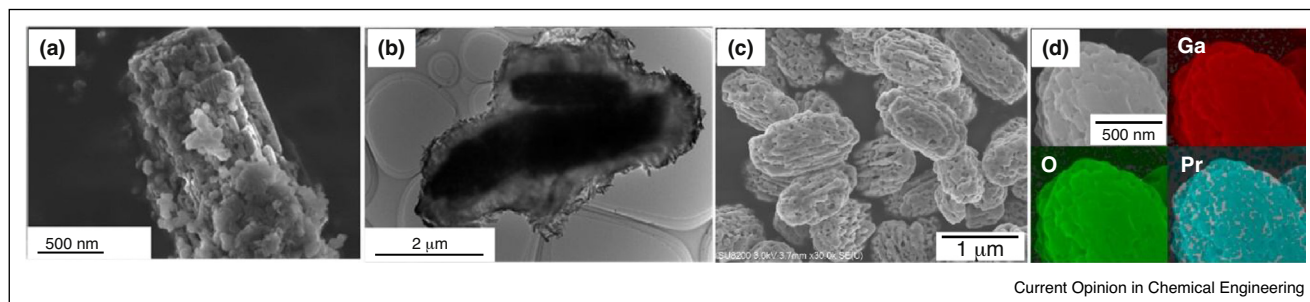
Increasing the number of active sites is another efficient way to enhance the photocatalytic activity for conversion of CO₂. As previously discussed, loading of co-catalysts has been widely used in the photocatalytic conversion of CO₂. Other strategies such as increasing the adsorption of CO₂ on the surface of Ga₂O₃ were shown to be useful and efficient for enhancing both the photocatalytic activity and selectivity toward CO evolution.

Iguchi *et al.* [47**] designed Mg–Al layered double hydroxide (LDH) modified Ga₂O₃ which showed drastically

improved the photocatalytic activity and selectivity toward CO for the conversion of CO₂ in and by H₂O using a 400 W Hg lamp. LDHs are thought to be good materials for the adsorption of CO₂ because of their surface basicity. Various kinds of LDHs have been reported to show photocatalytic activity for the conversion of CO₂ by Iguchi *et al.* and others [48–51]. A core–shell structure was observed in the 95 mol% Mg–Al LDH modification of commercial Ga₂O₃ nanorods (Figure 4a and b), which, upon loading 0.25 wt% Ag, showed the highest CO formation rate of 211.7 μmol h^{−1}. The selectivity toward CO evolution was determined to be 61.7%. It was suggested that the modification of the Mg–Al LDH also facilitates the selective transfer of photogenerated electrons from Ga₂O₃ to Ag particles to drive the conversion of CO₂ to CO.

Alkali, alkaline-earth, and rare-earth metal incorporated materials can be used as bases for the adsorption of CO₂ and play important roles in the surface capture of CO₂. Recently, Huang *et al.* [27**] reported that praseodymium-modified gallium oxide (Pr/Ga₂O₃) enhanced the photocatalytic activity and selectivity toward CO evolution in the conversion of CO₂ in and by H₂O using a 400 W Hg lamp as compared to that of bare Ga₂O₃. It was found that Pr(OH)₃ and Pr₂O₂CO₃ formed on the surface of Ga₂O₃ after calcination of the Pr precursor at high temperature in air. These Pr species were well dispersed on the spindle-like Ga₂O₃ nanoparticles after calcination (Figure 4c and d). Moreover, the Pr species facilitate CO₂ capture and storage in aqueous solution of NaHCO₃ with flowing CO₂. The formed Pr species with captured CO₂ decomposed to CO over the Ga₂O₃ photocatalyst with a Ag co-catalyst. Consequently, the Pr modified Ga₂O₃ exhibited much higher activity than that of the bare Ga₂O₃. Except Pr, modification of the surface of Ga₂O₃ with other rare-earth elements enhanced the evolution of CO, the selectivity toward CO also could be enhanced by further modification of the surface of the rare earth-modified Ga₂O₃ with Zn [52*].

Figure 4



SEM (a) and TEM (b) images of Mg-Al LDH modified Ga₂O₃. (c) Shows the Pr modified Ga₂O₃ and the corresponding elemental mapping image (d).

Reproduced from Ref. [47**] ((a) and (b)) and Ref. [27**] ((c) and (d)) with permission from The Royal Society of Chemistry.

Outlook

The development of efficient photocatalysts for the conversion of CO₂ is a great challenge but may help to solve the pressing issues of increasing CO₂ emissions and the energy crisis. The photocatalytic conversion of CO₂ using H₂O as an electron donor is a promising method to solve the two issues simultaneously. H₂O is an inexhaustible and clean electron source, which makes it an ideal choice to use for the fabrication of other highly valued chemicals such as carbon-based fuels and feedstocks. Ga₂O₃, as a wide bandgap photocatalyst, has sufficient reduction potential for the conversion of CO₂. However, the use of Ga₂O₃ is limited in the UV range, but still shows promise for further investigation at this stage. Modification of Ga₂O₃ with various dopants can enhance its photocatalytic activity and selectivity toward CO evolution. It is important to validate these methods and general strategies for the improvement of activity and selectivity of gallium oxide-based catalysts.

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